



Efficient reduction of CO₂ to C₂ hydrocarbons by tandem nonthermal plasma and photocatalysis

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ABSTRACT

CO₂ photoreduction to hydrocarbons is a carbon-neutral technology for renewable energy. However, this strategy is challenged by the thermodynamic stability of CO₂ and the low efficiency of multi-photoelectron utilization. In this paper, tandem nonthermal plasma and photocatalysis were used to effectively improve the efficiency of CO₂ reduction to C₂. We first activated CO₂ by nonthermal plasma technology (NTP) and then converted the activated CO₂ into C₂ products by Cd_{0.8}Zn_{0.2}S/In₂O₃ photocatalyst with a special nanostructure. Without the addition of any sacrificial agent, the C₂ yield of the catalyst reached 0.382 μmol h⁻¹, which is one of the highest performances to date. In situ experimental and computational studies show that CO₂⁺ activated by NTP has higher π orbital and HUMO levels of lone pair electrons and promotes the reduction of CO₂⁺ by injecting electrons into the vacant orbital of the active site of Zn. At the same time, the unique structure of Cd_{0.8}Zn_{0.2}S/In₂O₃ photocatalyst can extend the life of charge through the optical field enhancement effect, and then react with the CO₂⁺ intermediates generated by NTP technology to promote the coupling of C-C bonds, and finally promote the photocatalytic multi-electron reaction to produce C₂ hydrocarbons.

1. Introduction

Photocatalytic conversion of CO₂ into multi-carbon fuels is considered one of the potential green ways to ease the pressure on global energy demand [1]. However, the formation of valuable hydrocarbons requires the activation of stable CO₂ (750 kJ/mol) and then undergoes a multi-electron C-C coupling process. At present, the main products of photocatalytic CO₂ reduction reaction are usually C₁, such as CO, CH₄, and other products. C₂ hydrocarbons, such as ethylene and ethane, remain challenging. To date, many studies have focused on promoting the yield of multi-carbon products by constructing photocatalysts with multi-electron supply capability and surface active sites to promote the C-C coupling reaction of C₁ intermediates [2]. Although these effective strategies are effective in the generation of C₂ products, the critical step of CO₂ activation is often ignored [3,4]. The product of CO₂ activation can act as a C₁ intermediate to promote the C-C coupling reaction. Therefore, the CO₂ reduction efficiency can be improved more effectively by activating CO₂ first and then reducing it through a photocatalytic reaction.

Non-thermal plasma technology (NTP) is also an effective way to convert CO₂ into high-value-added chemicals [5–7]. The primary

mechanism of NTP consists of creating an electric field by applying a potential difference between parallel plates. Under the action of an electric field, CO₂ gas is easily activated by high-energy electrons to produce short-lived species, such as excited state species, free radicals, electrons, and the long-lived CO and CO₂⁺ charged gas at room temperature [8,9]. Although NTP is easy to activate stable CO₂ molecules, there are some limitations, such as the reaction products are mostly C₁ products and low selectivity [10–12]. In addition, the lack of hydrogen protons in the NTP system (pure CO₂ gas) prevented the synthesis of target C₂ hydrocarbon products [13]. Therefore, a potential strategy is to first convert thermodynamically stable CO₂ into more active charged matter (CO₂⁺) through NTP technology, and then reduce activated CO₂ by designing efficient photocatalysts [14]. Accordingly, photocatalysts with multi-electron supply capabilities are essential for realizing the above reaction. This creates extra demands on the photocatalysts, that is, to prolong the photoelectrons' lifetime for CO₂⁺ reduction to C₂ products (CO₂⁺+12e⁻→C₂H₄+H₂O; CO₂⁺+14e⁻→C₂H₆+H₂O). Currently, the excitation lifetime timescales for photoelectrons are typically 1–10 ns in bulk photocatalysts and are comparable to the recombination timescale. The multielectron C₂ synthesis process is challenging in such a tiny lifetime of photoelectrons. To solve this conundrum, controlling

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the photocatalyst's excited state is critical to enhancing the average excitation lifetime. Many valuable strategies have recently been explored; the most successful ones tend to design nanostructures to achieve the maximum absorption of photons; nanocavity structures provide a great example [15]. The unique structure could promote photoelectrons transition from the ground state (S_0) to a higher level (S_x), resulting in longer charges' lifetime. At the same time, the long-lived photoelectrons can gather at the metal active sites, reacting with $^*CO_2^+$ produced by NTP to form C_2 products, ultimately fulfilling the NTP-assisted photocatalytic CO_2 reduction process [16,17].

In the reported photocatalysts, transition metal-based catalysts (e.g., Cu, Ni, Zn) exhibit high activity, stability and longer electrons lifetimes for CO_2 adsorption and reduction. It is due to the unsaturated coordination (3d or 4 s orbitals), more positive Fermi level position, and unique electronic local structure. Among these transition metals, Zinc-based nanomaterials can be used as active centers for photocatalytic CRR. This can be ascribed to the unsaturated 4 s orbit, which can accept electrons on the delocalized π bond of CO_2^+ . Taken together, the rational design of Zinc-based nanoconfined photocatalysts for NTP-assisted CO_2 conversion into C_2 products is essential.

Here, a $Cd_{0.8}Zn_{0.2}S/In_2O_3$ photocatalyst with a unique nanostructure was synthesized by nanostructure engineering. We activated stable CO_2 to CO_2^+ using non-thermal plasma technology, and then efficiently converted CO_2^+ to C_2 products via this $Cd_{0.8}Zn_{0.2}S/In_2O_3$ photocatalyst. The system provides high C_2 productivity of $0.382 \mu mol h^{-1}$ without any sacrificial agent. In situ experimental and computational studies show that the unique structure of $Cd_{0.8}Zn_{0.2}S/In_2O_3$ photocatalyst can promote the transition of photoelectrons from the ground state (S_0) to a higher energy level (S_x), and extend the lifetime of charge through optical field enhancement effect [18]. At the same time, long-lived photoelectrons can gather at the metal active site and react with CO_2^+ intermediates generated by NTP technology to promote the coupling of C-C bonds, and finally promote the photocatalytic multi-electron reaction to produce C_2 hydrocarbons.

2. Experimental section

2.1. Chemicals and materials

Indium nitrate ($In(NO_3)_3$, 99 %), 1, 4-benzenedicarboxylic acid ($C_8H_6O_4$, 98 %), N, N-dimethylformamide (C_3H_7NO , DMF, 99 %), Zinc nitrate ($Zn(NO_3)_2$, 99 %), Cadmium chloride ($CdCl_2$, 99 %), thioacetamide (CH_3CSNH_2 , 99 %). Polyvinylpyrrolidone (PVP, average mol wt 10,000) was purchased from Sinopharm Chemical Reagent Co, Ltd. Ethanol was purchased from Sigma-Aldrich. The deionized water was obtained from a water purification system (OSJ-UP). All the chemical reagents were used as received without further purification.

2.1.1. Synthesis of In-MIL-68 prisms

The In-MIL-68 prisms was synthesized by a solvothermal method. In a typical reaction, 120 mg of $In(NO_3)_3$ and 120 mg of 1, 4-benzenedicarboxylic acid were dissolved in 60 mL of DMF and stirred for 30 min. Then the above solution was transferred in an oil bath at $130^\circ C$ for 40 min. After the solution was cooled down to nature temperature, the precipitate was washed with deionized water and ethanol several times and dried at $60^\circ C$ for 4 h.

2.1.2. Synthesis of $Cd_{0.8}Zn_{0.2}S$ photocatalysts

In a typical reaction, 0.36 g of $CdCl_2$, 0.04 g of $Zn(NO_3)_2$ and 0.18 g of thioacetamide were dissolved in 60 mL of deionized water and stirred for 30 min. Then the above solution was transferred in an oil bath at $180^\circ C$ for 2 h. After the solution was cooled to natural temperature, the precipitate was washed with deionized water and ethanol several times and dried at $60^\circ C$ for 4 h, labeled as CZS.

2.1.3. Synthesis of In_2O_3 solid rods

Typically, the as-obtained In-MIL-68 prisms were annealed in air at $500^\circ C$ for 25 min with a heating rate of $4^\circ C min^{-1}$, and then the product was washed with deionized water three times, dried in $60^\circ C$ for 4 h, labeled as In-1.

2.1.4. Synthesis of nanoconfined In_2O_3 photocatalysts

Typically, the as-obtained In-MIL-68 prisms were annealed in air at $500^\circ C$ for 60 min with a heating rate of $2^\circ C min^{-1}$, and then the product was washed with deionized water three times, dried in $60^\circ C$ for 4 h, labeled as In-2.

2.1.5. Synthesis of solid $Cd_{0.8}Zn_{0.2}S/In_2O_3$ photocatalysts

In a typical procedure, a 200 mg In-1 sample was dissolved in 40 mL deionized water and stirred for 30 min. A certain amount (2 wt%) of Zn (NO_3)₂, $CdCl_2$, and thioacetamide was added, and the mixture was vigorously stirred for 30 min at room temperature. The mixture was transferred to a 100 mL Teflon-lined stainless-steel autoclave, which was heated to $180^\circ C$ for 3 h. When the autoclave was cooled down to room temperature, the mixture was washed with deionized water and ethanol several times, then dried at $60^\circ C$ for 4 h, labeled as InCZ-1.

2.1.6. Synthesis of nanoconfined $Cd_{0.8}Zn_{0.2}S/In_2O_3$ photocatalysts

In a typical procedure, a 200 mg In-2 sample was dissolved in 40 mL deionized water and stirred for 30 min. A certain amount (2 wt%) of Zn (NO_3)₂, $CdCl_2$ and thioacetamide was added, and the mixture was vigorously stirred for 30 min at room temperature. The mixture was transferred to a 100 mL Teflon-lined stainless-steel autoclave, which was heated to $150^\circ C$ for 3 h. When the autoclave was cooled down to room temperature, the mixture was washed with deionized water and ethanol several times, then dried at $60^\circ C$ for 4 h, labeled as InCZ-2.

2.2. Characterizations

Various instruments were used to measure the experimental products. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) were performed for obtaining TEM, SEM, and EDS maps. A power X-ray diffraction measurement was performed on the samples (Lab X XRD-6100, SHIMADZU) in order to determine their crystal phase. A temperature programmed desorption (TPD, MICROMERITICS AutoChem II 2920) was executed on the as-prepared samples to quantify the adsorption and desorption characteristics of both CO_2^+ and CO. An electron spin resonance (ESR) analysis, utilizing the Bruker EMX PLUS, was carried out on the CZS and InCZ-2 samples to evaluate the presence of free radicals during photocatalytic reactions. An integrating sphere attachment was used to measure UV-vis diffuse reflectance spectra using a UV-vis spectrophotometer (UV-2600, SHIMADZU). The femto-second transient absorption spectrum (Helios) was used to measure the ultrafast dynamics of photoexcited charge transfer. An in situ super-resolution confocal microscope (Leica TCS SP8 STED 3X) was used to determine the transient light absorption and fluorescence signal of as-prepared samples. The fluorescence signals of catalysts were measured using an SEM-Raman (Renishaw Raman spectrometer) system and surface-enhanced Raman spectroscopy. Time-resolved fluorescence spectrophotometers (Edinburgh Instruments, FLS980) were used to measure the fluorescence signal and steady-state photoluminescence (PL) spectra at wavelengths of 365 nm and 540 nm. A solid junction apparatus analyzed the surface photovoltage spectra of samples with a light source-monochromator-lock-in detection measurement at 298 K. Data were collected from triple-prism monochromators (Hilger and Watt, D300) with amplification (Brookdeal, 9503-SC). All the surface photovoltage spectra were measured with an ITO electrode film. A Shamrock 750 emission spectrometer obtained the emission spectra. With a CHI660E electrochemical apparatus (Shanghai, China), the electrochemical photocurrent and impedance spectra were measured

using a standard three-electrode cell. This consisted of a working electrode with a platinum wire counter and Ag/AgCl reference electrode. As a working electrode, FTO film was used to test the Mott-Schottky spectra. The electrolyte used in all electrochemical measurements was 1.0 M Na₂SO₄. A high-resolution confocal microscope (Leica TCS SP8 STED 3X) was used to obtain super-resolution confocal spectra and images. An inVia Qontor Raman spectrum was used to obtain Raman spectra and mapping data.

2.3. In situ FTIR experiment

In situ reaction cells were typically filled with 2 mg of the photocatalyst and purged with CO₂ gas treated by NTP for 1 h. Then 0.2 mL ultra-pure water was added to the reaction cell. An FTIR spectrophotometer Nicolet iS50 was used to carry out the in situ FTIR measurement at room temperature.

2.4. In situ Raman experiment

In situ Raman spectroscopy was conducted using Renishaw Raman spectrometers with NTP active CO₂ as the feeding gas. A mixture of 2 mL of ultra-pure water and 10 μ L of Nafion solution (10 wt%) was sonicated for 10 min to form a homogeneous solution containing 2 mg of the prepared photocatalysts. The above solution was uniformly coated on a 0.5 \times 0.5 cm² FTO film and then dried at 60 $^{\circ}$ C for 12 h to obtain the as-prepared samples for in situ Raman spectroscopy.

2.5. FDTD simulations details

Finite-difference time-domain simulations (FDTD) were obtained using Lumerical FDTD Solutions. The geometry of photocatalysts was modeled as hollow hexagonal prisms and solid hexagonal prisms; hollow hexagonal prisms contain clusters inside and hollow hexagonal prisms with particles on the surface. The height of the hexagonal prism was 4 μ m, and the refractive index of In₂O₃ and Cd_{0.8}Zn_{0.2}S was 1.23 and 1.4, respectively. A normal plane wave illuminated the structure. Along the Y-axis, plane wave polarized light with a wavelength ranging from 200 to 800 nm was used. The mesh override region was set to 0.3 nm for minimum simulation time and maximum field enhancement resolution, and the overall simulation time was 200 fs.

2.6. DFT computational details

The plane-wave pseudopotential method depending on density functional theory was used in the first principles calculations. The geometry optimizations and electron structure were adopted by the Vienna Ab initio Simulation Package (VASP), and the electron exchange and correlation potentials were employed by a generalized gradient approximation with the Perdew-Burke-Ernzerhof exchange-correlation functional in VASP code. The van der Waals (vdW) interactions were described using the empirical correction in Grimme's scheme (DFT + D2). Energetics calculations for reaction mechanisms were carried out by using spin-polarized density functional theory (DFT). The A plane-wave cut-off energy of 420 eV was adopted. The heterojunction structure Cd_{0.8}Zn_{0.2}S/In₂O₃ is used and the calculation model is composed of 127 atoms. Combining with XRD and HRTEM analysis, (101) surface of Cd_{0.8}Zn_{0.2}S lattice is used as reaction plane. A Monkhorst-Pack 5 \times 4 \times 1 k-point grid was adopted to sample the Brillouin zone and the vacuum space was 25 \AA . Structure optimization calculations were done until the total energy changes were within 1 \times 10⁻⁵ eV per atom and the Hellmann-Feynman force on each atomic site was less than 0.05 eV/ \AA . All Gibbs free energy values were referenced to the computational hydrogen electrode (CHE) model using the proton-coupled electron transfer (PCET) approach. The chemical potential of the H⁺/e⁻ pair was considered as half of the H₂ gas molecule. The ΔG value was obtained via the formula: $\Delta G = \Delta E + \Delta ZPE - T\Delta S$, where ΔE is the reaction

energy difference between the product and reactant occurring on catalysts. ΔZPE and ΔS are the changes in zero point energies and entropy at 298.15 K, which were calculated via considering only the vibrational frequencies.

3. Results and discussion

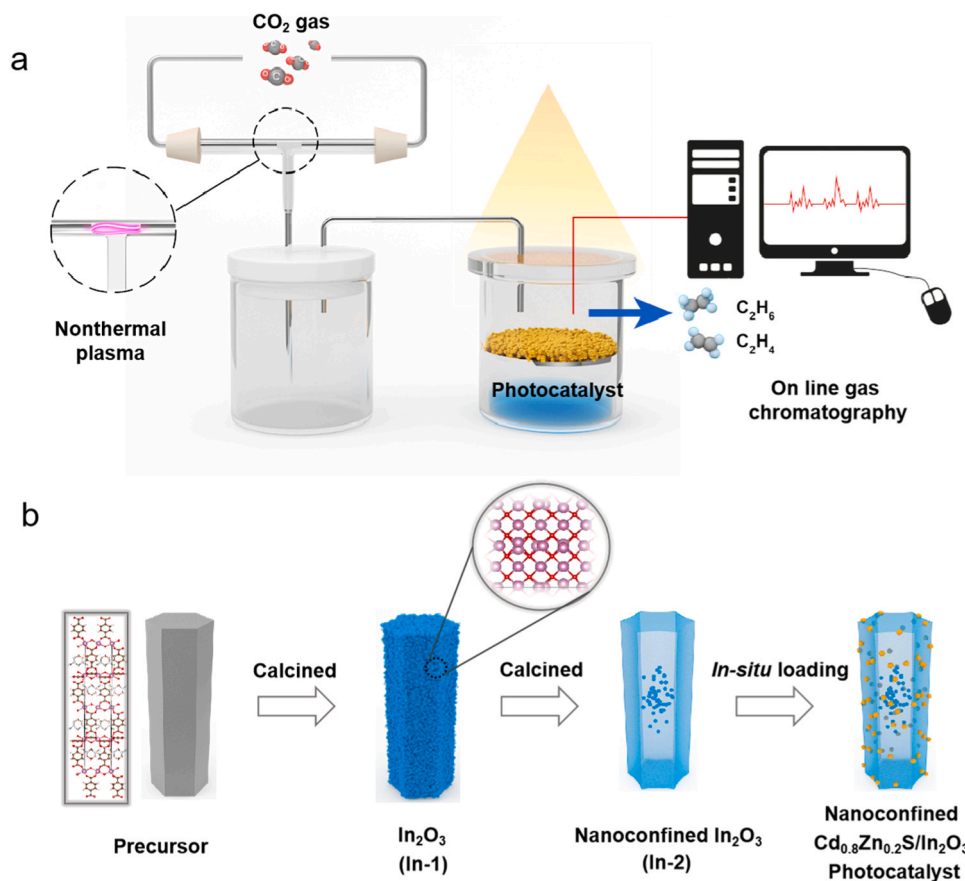
3.1. The NTP-assisted photocatalytic CO₂ reaction system and microstructures of photocatalysts

We first proposed to activate CO₂ by coupling a nonthermal plasma process in series integration to generate reactive CO₂⁺ to achieve the efficient photocatalytic synthesis of ethane and ethylene (Scheme 1a, Fig. S2, Supporting information). Understanding the pCRR process relies heavily on determining CO₂ products activated by NTP. In situ emission spectra in Fig. S3a detect the gas after the NTP discharge. When high-energy electrons collide with CO₂ molecules, ionization occurs, and a large number of CO₂⁺ and CO are produced. To determine the stability of CO₂⁺, according to Fig. S3b, in situ emission spectra indicate that CO₂⁺ charge gas can survive for a long time with NTP on. Upon turning off NTP, however, the CO₂⁺ signal value will disappear within approximately 190 s (Fig. S3c). Thus, we used an in-situ reaction method to provide CO₂⁺ continuously by turning on NTP to activate CO₂ during the photocatalytic reaction. To favour multielectron proton reduction of the CO₂⁺ reaction, a nanoconfined Cd_{0.8}Zn_{0.2}S/In₂O₃ photocatalyst is rationally developed.

A discussion of the synthesis of photocatalysts is then presented. The In₂O₃ nanorod (labeled as In-1, Fig. S4) is prepared with the In-based organic framework nanocrystal in Fig. 1a. Afterward, the precursor is calcined in air to obtain a hollow In₂O₃ nanorod with a cluster inside (labeled as In-2, Fig. S5). In-situ loading a 2 wt% Cd_{0.8}Zn_{0.2}S on the surface of In₂O₃ nanorod to obtain the nanoconfined photocatalyst (labeled as InCZ-2, Scheme 1b). In Fig. S6, pure Cd_{0.8}Zn_{0.2}S and Cd_{0.8}Zn_{0.2}S/In₂O₃ bulk material is also synthesized for comparison with the nanoconfined photocatalyst (labeled as CZS and InCZ-1). Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM) images of InCZ-2 are shown in Fig. 1b, c and Fig. S7. The InCZ-2 photocatalyst has the structure of a hollow hexagonal prism, and the nanocluster is seen clearly to be encapsulated in the internal cavity. The Cd_{0.8}Zn_{0.2}S nanoparticles are uniformly anchored outside the In₂O₃ surface. Subsequently, a high-resolution TEM image (HRTEM) exhibits that InCZ-2 has a heterojunction structure (Fig. 1d). The crystallized inner materials with a lattice space of 0.292 nm correspond to the (222) facet of In₂O₃ [19]. The outside nanoparticle crystal planes can be studied using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). As shown in Fig. 1e, the lattice size of nanoparticles can match 0.316 nm, corresponding to the (101) crystal plane of Cd_{0.8}Zn_{0.2}S. The formation of InCZ-2 is further confirmed by X-ray diffraction (XRD) in Fig. 1f. The distribution of In, Cd, Zn S, and O elements is examined by an energy-dispersive spectrometer (EDS) mapping and X-ray photoelectron spectroscopy (XPS) in Fig. 1g, Fig. S8 and Table S1.

3.2. The characterization of energy band structure and NTP-assisted photocatalytic CO₂ reduction performance

A common goal among researchers is the development of valuable C₂ products using as-prepared photocatalysts. As part of a solar-driven reduction process, photoexcited electrons in a photocatalyst's conduction band (CB) can convert CO₂ into C₂ carbonaceous fuels. That is to say, the conduction band position of as-prepared photocatalysts is crucial to photosynthesize C₂ products. It can be seen from Fig. S9 that the energy gap between In₂O₃ and Cd_{0.8}Zn_{0.2}S is 2.32 and 2.0 eV, respectively. Besides, a flat band potential (V_{fb}) for In₂O₃ is estimated to be -0.40 eV, while that for Cd_{0.8}Zn_{0.2}S is estimated to be -0.35 eV



Scheme 1. a) NTP-assisted photocatalytic CO₂ reduction process. b) Schematic illustration of the fabrication of nanoconfined Cd_{0.8}Zn_{0.2}S/In₂O₃ photocatalyst.

(Fig. S10). From the semiconductor energy gap formula ($E_g = V_{\text{band}} - V_{\text{fb}}$), we can deduce that In₂O₃ and Cd_{0.8}Zn_{0.2}S exhibit VB values of 1.92 and 1.65 eV, respectively. Photoexcited electrons are transferred to the Cd_{0.8}Zn_{0.2}S surface for CO₂ reduction. Thus, the CB photoelectrons of Cd_{0.8}Zn_{0.2}S can reduce CO₂ into C₂H₄ and C₂H₆ according to the photocatalytic reduction potential diagram (Fig. S11).

Our immediate concern is whether the nanoconfined catalysts exhibit the high NTP-assisted photoreduction activity of CO₂. In the first step, we use the In-2 catalyst to test the yields of ethylene and ethane at different plasma voltages. Fig. S12a illustrates that the In-2 catalyst exhibits the maximum activity for the C₂ product when the plasma voltage is 50 V, and its activity gradually declines with increasing voltage. This may indicate that under high voltage, the high energy electrons in the plasma electric field are more likely to react inversely with CO₂⁺ and change back to CO₂ gas ($e^- + \text{CO}_2^+ \rightarrow \text{CO}_2$), resulting in a significant decrease in subsequent photocatalytic activity. Moreover, we investigated the effect of different discharge tip distances on the photocatalytic activity. Fig. S12b illustrates that when the discharge tip distance is 2 mm, the residence time of CO₂ gas in the plasma action area is shortened, resulting in a lower concentration of CO₂⁺ and, consequently, a lower photocatalytic activity. With an increase in tip distance to 4 mm, plasma interaction intensity increases, exhibiting photocatalytic performance. However, as the tip distance increases to 6 mm, inert CO₂ cannot effectively activate, causing CO₂ photocatalytic activity to decrease. Therefore, the photocatalytic CO₂ reduction activity was then tested under 50 V plasma voltage and 4 mm discharge tip distance for the other prepared samples.

As a first step, we examined the pCRR activity of photocatalysts without nanostructures under NTP conditions. As shown in Fig. 2a, the InCZ-1 sample shows the great performance in delivering C₂ hydrocarbons rates of 0.219 μmol h⁻¹, which are 3.8 and 2 times that of the CZS

and In-1 samples. As shown above, the addition of Cd_{0.8}Zn_{0.2}S (CZS) to In₂O₃ significantly enhanced pCRR's performance. There is, however, still a low level of C₂ product activity. Thus, we assessed the pCRR activity of photocatalysts in nanoconfined structures. As expected, the InCZ-2 sample exhibited better pCRR performance with a high C₂ hydrocarbons-evolution rate of 0.382 μmol h⁻¹ (Fig. 2b). It should be noted that the InCZ-2 sample can maintain C₂H₄ and C₂H₆ selectivity at 15.4 % and 82.6 %, respectively (Fig. S13a, b). Nevertheless, there was a significant reduction in the selectivity of the photocatalytic C₂ products produced by the In-2 sample (7.2 % for C₂H₄ and 47.8 % for C₂H₆). It could be attributed to different active sites on the photocatalysts, which can impact adsorption and desorption, as well as reaction intermediates. In addition, the InCZ-2 sample produced oxygen during the pCRR process with NTP assistance (Fig. S13c). As is evident from the above results, the nanoconfined structure photocatalyst is indeed capable of promoting the generation of C₂ products. Furthermore, the pCRR stability test for the InCZ-2 sample is conducted under the same experimental conditions, which reveals a slight decrease in activity over 5 cycles due to washing the photocatalyst after each cycle (Fig. 2c). After cycle-run experiments, the SEM image and XRD pattern of the InCZ-2 sample maintains the original morphology and the main characteristic peaks (Fig. S14). This may be attributed to the special structure of the InCZ-2 sample, in which photogenerated holes react with hydroxyl groups (OH⁻) in the photocatalytic reaction, resulting in the formation of hydroxyl radicals (·OH), which are combined to produce hydrogen peroxide, and then decompose to produce O₂ during the photocatalytic reaction. During this process, photocorrosion of InCZ-2 sample can be greatly suppressed by this process. For the purpose of proving the validity of the above mechanism, we conducted a capture experiment of in situ hydroxyl radicals. As shown in electron spin resonance (ESR) spectra (Fig. S15), a characteristic quartet of peaks (1:2:2:1) associated

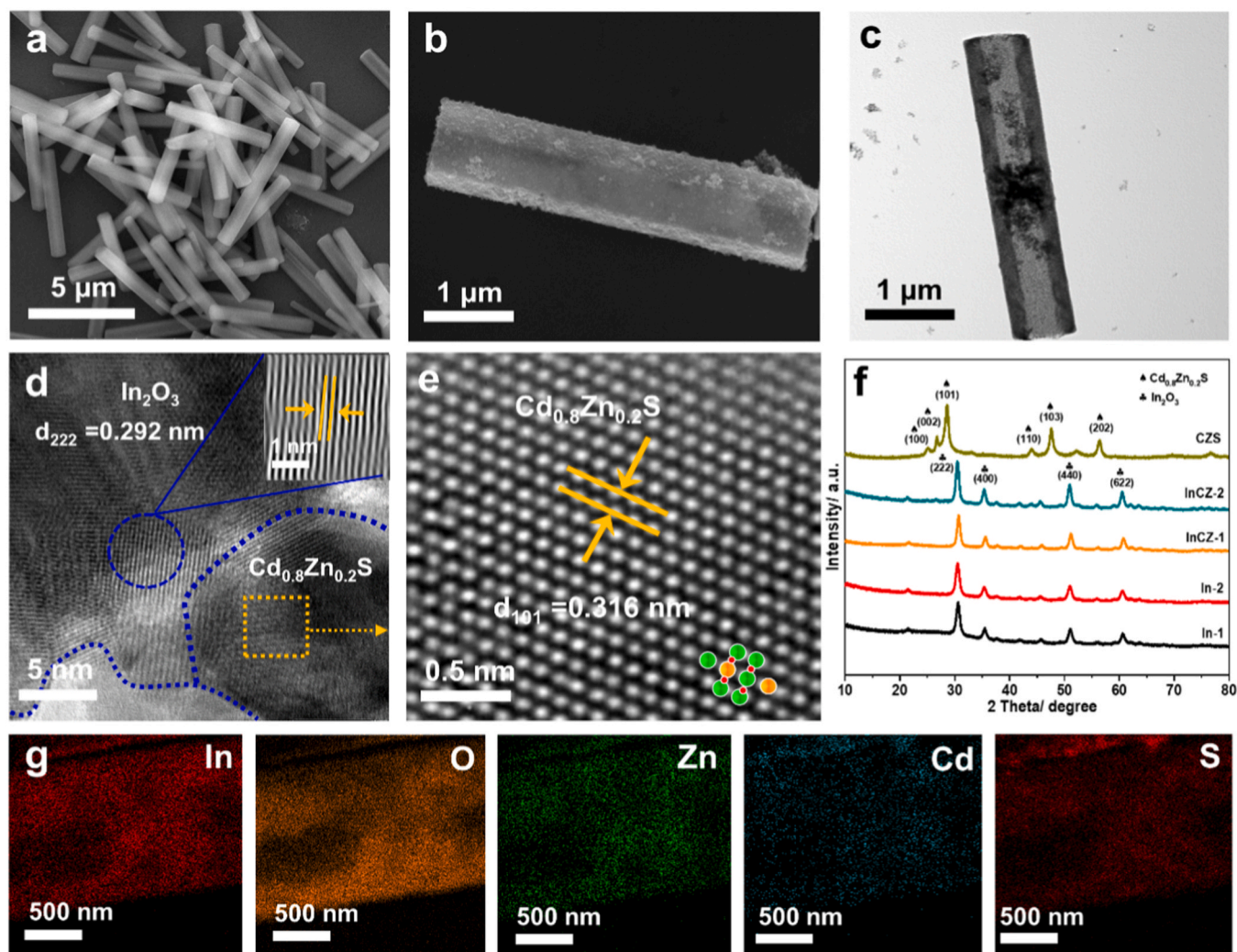


Fig. 1. a) SEM image for MIL-68 template. b, c) SEM and TEM images for InCZ-2. d) high-resolution TEM image for InCZ-2 (inset, the selected area electron diffraction pattern). Atom key: Cd (green), Zn (orange), S (red). e) Aberration-corrected HAADF-STEM image for (101) crystal plane of InCZ-2. f) XRD patterns for as-prepared samples. g) EDS mapping results for InCZ-2.

with the 5,5-dimethyl-1-pyrroline-*N*-oxide-OH (DMPO-OH) radical adduct is immediately detected after 80 s light irradiation. ESR results indicate that the InCZ-2 sample can generate hydroxyl radicals in the NTP-assisted photocatalytic CO₂ reduction reaction, which is the key intermediate for the formation of O₂. Conversely, there are no characteristic peaks of hydroxyl radicals for CZS sample, indicating that holes are likely to cause corrosion of the catalysis, resulting in poor photocatalytic stability. These results demonstrate excellent photocatalytic stability for InCZ-2. According to Fig. 2d, the maximum QE% for C₂H₄ and C₂H₆ in the InCZ-2 sample is 1.15 % and 1.65 %, which is higher than that of the In-1 sample (0.13 % and 0.46 %). More importantly, we have measured CRR activity under an Ar atmosphere with illumination or under CO₂ plasmas without illumination to exclude C₂H₄ and C₂H₆ contaminants. In the above reaction system, neither C₂H₄ nor C₂H₆ is detected by gas chromatography, which establishes that there are no C₂ product contaminants (Fig. S16). Besides, as photocatalytic H₂ evolution reaction is a competitive reaction, the same conditions are used to measure it. As shown in Fig. S17, there is no detection of H₂ because only water serves as a proton in the reaction system without any sacrificial agent [20,21]. Furthermore, to eliminate the influence of CO gas after plasma treatment, we also measured the photocatalytic activity of CO or CO₂/CO mixture as the feeding gas. As shown in Fig. S18, the prepared samples exhibit a low photocatalytic synthesis rate of ethylene and

ethane (within the error range), which indicates that the synthesis of photocatalytic C₂ products cannot be enhanced by a large amount of CO generated by plasma, whereas CO₂⁺ is critical to ethylene and ethane synthesis [22,23].

3.3. Optical and electrochemical properties

A further understanding of how the nanoconfined structure photocatalyst strengthens the multielectron reduction process. In-situ spectrum and finite-difference time-domain (FDTD) calculations of the as-prepared photocatalysts are conducted. As shown in Fig. 3a and Fig. S19, the surface-enhanced Raman spectroscopy (SERS) mapping test of the InCZ-2 and In-1 samples are compared. At 400 nm excitation wavelength, InCZ-2 exhibits a roughly 2-fold enhancement in SERS signal compared to bulk In-1. This difference could be attributed to the nanocavity structure, and the rough surface exhibits a light field enhancement effect (LFE) [24].

In order to eliminate tablet pressing errors caused by the powdered catalyst. An SEM-Raman system analysis of InCZ-2 and In-1 samples is carried out to determine the effects of nanoconfined structures on LFE (Fig. 3b and Fig. S20). As can be seen, the Raman scattering light signal is gathered on the surface of the nanoconfined InCZ-2 sample and shows a strong Raman signal peak in the range of 350–600 nm wavelength [25,

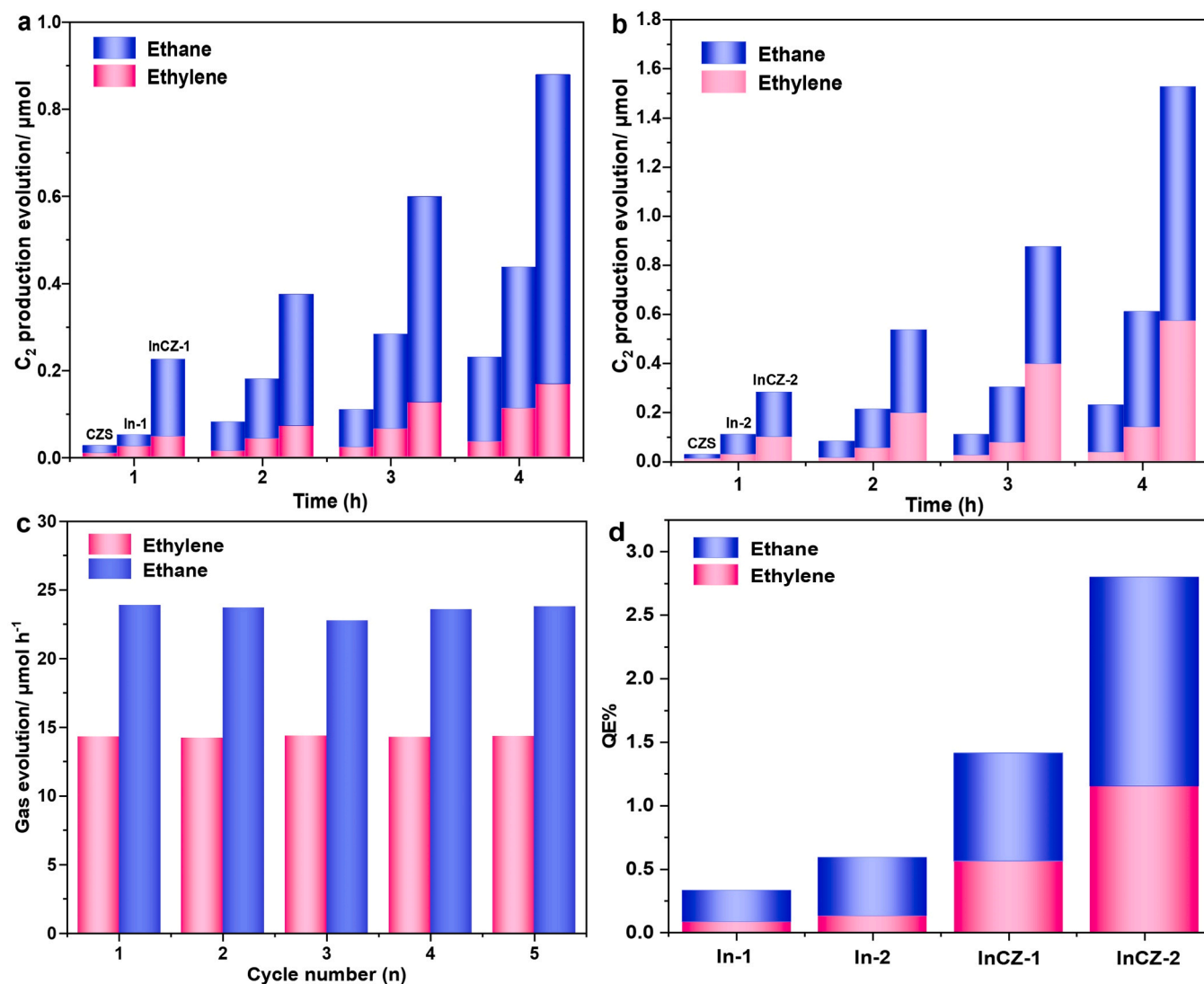


Fig. 2. a, b) C₂H₄ and C₂H₆ evolution for the as-prepared samples. c) Cycling run test for the InCZ-2 sample. d) Wavelength dependence of the apparent quantum yield for InCZ-2 sample.

26]. According to the evidence above, the nanocavity and rough surface structure are able to initiate the LFE effect, which enhances light absorption by the catalyst. Further, UV-vis spectroscopy and photoluminescence spectra confirm the above results in Fig. S21 and S22. The aforementioned experimental phenomenon can be verified by FDTD of the as-prepared photocatalysts are simulated (In-1, In-2, InCZ-1, and InCZ-2) [27,28]. For optical simulation, an ellipsometer is used to measure the refractive index of In₂O₃ and Cd_{0.8}Zn_{0.2}S (Fig. S23). Through simulation of a catalyst model (InCZ-2) exposed to full light, it can be observed that the light field inside the nanocavity and around the catalyst surface particles is enhanced (Fig. 3c). The bulk (In-1 and InCZ-1) or nanoconfined structure without surface particles (In-2), however, only exhibits a weak light signal on the photocatalyst surface (Fig. S24). As evidenced by spectrum tests and FDTD simulations, the presence of the inner cavity and surface particle structure could increase the near light field to boost light photons absorption of the photocatalyst. When the catalyst absorbs photons, photoelectrons are excited to participate in the multielectron reduction reaction. Thus, photoelectron lifetime plays a critical role in multielectron reduction reactions. For this reason, the fluorescence lifetime of the as-prepared samples is measured using in situ super-resolution confocal microscope fluorescence. The In-1 sample only displays a dim fluorescence signal on its surface (Fig. 3d). However, Fig. 3e and Fig. S25 show that the InCZ-2

sample has a regular nanoconfined structure and emits an extremely bright fluorescence signal. Furthermore, transient light absorption spectra with the NTP generator provide additional evidence for this conjecture (Fig. 3f). In a CO₂⁺ ion atmosphere, the InCZ-2 sample shows the highest values in transient absorption signals, markedly surpassing the In-1 and In-2 samples by three and two-fold, respectively. Additionally, the light absorption intensity of the InCZ-1 sample loaded with CZS nanoparticles was also improved as compared to the pure In₂O₃ samples (In-1 and In-2). These experimental results affirm the capacity of nanoconfined structures and heterojunctions to enhance material light absorption efficiency significantly. Also, Fig. 3g provides transient fluorescence spectra (TF) of InCZ-2 and In-1 samples that can be used to calculate the fluorescence lifetimes for comparison. In the short lifetime of excited carriers, it decreases from 1.10 ns (In-1) to 0.039 ns (InCZ-2), while in the long lifetime, it improves from 24.15 to 122.29 ns. In view of this, In-1 and InCZ-2 samples have average fluorescence lifetimes ($\tau_{\text{avg}} = \tau_1 \times \text{rel \%} + \tau_2 \times \text{rel \%}$) of 25.2 and 122.3 ns, respectively (Table S2). The raw data of the TF can be viewed in Fig. S26. Through the above experimental results, structure-induced enhancement of light fields may be responsible for the large increase in fluorescence lifetime. The experimental results described above are in accordance with the results of the FDTD simulation.

To understand why fluorescence lifetime increases, the Femtosecond

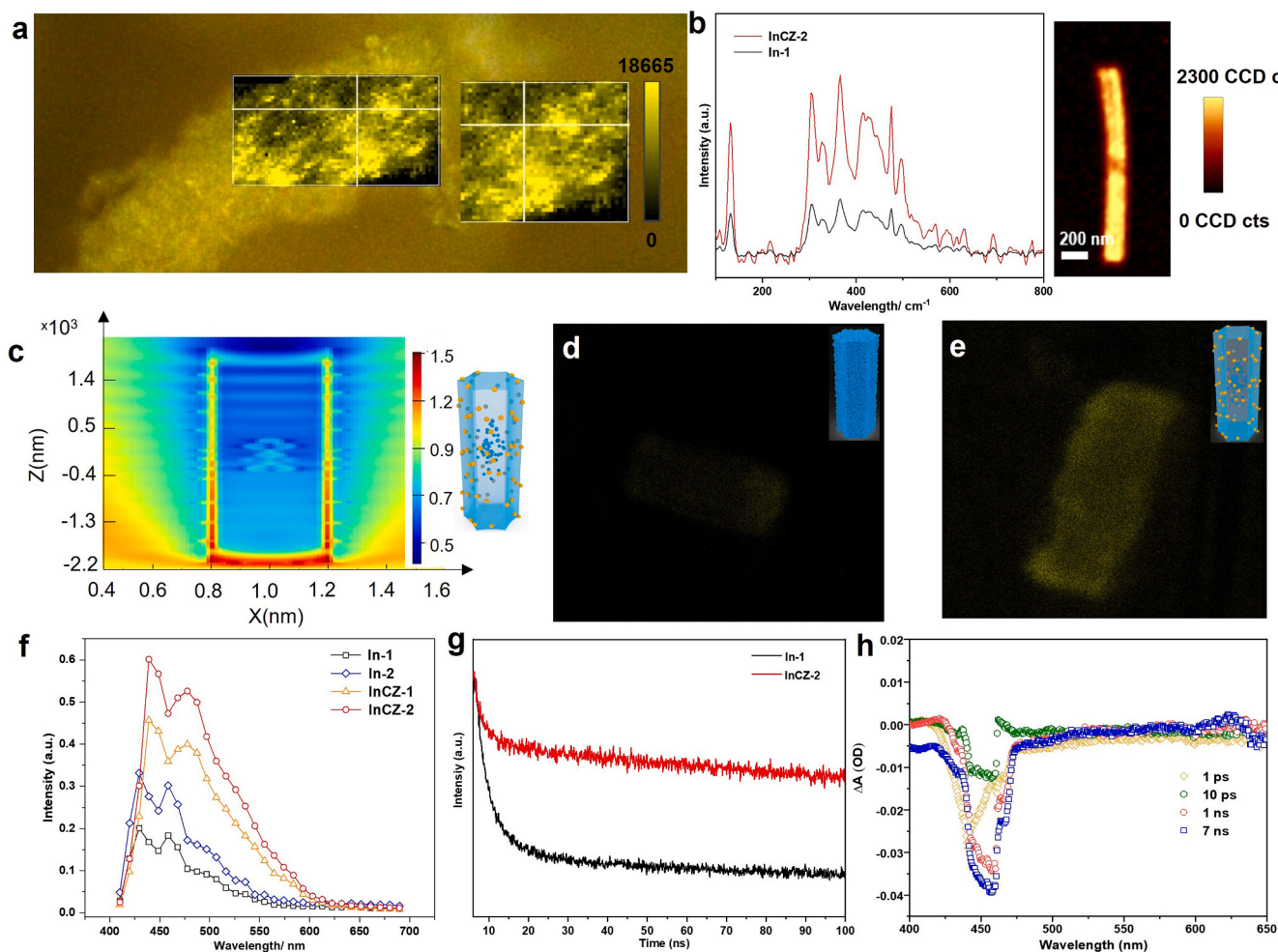


Fig. 3. a) SERS mapping test of the InCZ-2 sample. b) The SEM-Raman system analysis of the InCZ-2 and In-1 samples (Inset, the SEM-Raman signal mapping of the InCZ-2 sample). c) FDTD simulation of the InCZ-2 mode. d, e) In situ super-resolution confocal microscope fluorescence of In-1 and InCZ-2 samples. f) Transient light absorption spectra of In-1 and InCZ-2 samples. g) Transient fluorescence spectra of In-1 and InCZ-2 samples. h) Femtosecond transient absorption spectrum of the InCZ-2 sample.

transient absorption spectrum (fs-TA) is measured to monitor the ultrafast dynamics of photoexcited charge transfer. As shown in Fig. 3h and Fig. S27, InCZ-2 exhibits a bleach band peaking at 465 nm due to the 1st excitonic bleach for inner In_2O_3 . The shifted bleach band may be due to $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ growth on the In_2O_3 surface. There is a broad positive absorption band between 475 nm and 650 nm. This may result from the excitonic bleach for $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ particles (Fig. S28) [29]. Furthermore, an investigation of transient photocurrent responses is conducted. Fig. S29 shows that the InCZ-2 sample exhibits a more robust photocurrent response than the other samples, indicating that the heterojunction structure could enhance electron-hole separation. According to Fig. S30, the surface photovoltaic spectrum and interface resistance test confirm the same experimental results. Taken together, due to the LFE effect caused by the nano inner cavity and surface particle structure, resulting in a substantial increase in the absorption of light. Moreover, photoelectrons migrate from the inner layer of In_2O_3 to the surface of $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$, where they relax back to the ground state, greatly extending the life of photoelectrons. This process can prolong photoelectron life and continuously provide electrons in subsequent multielectron reactions.

3.4. Mechanism of photocatalytic CO_2 reduction

Additionally, with CO_2^+ as the primary reactant, achieving efficient adsorption of CO_2^+ is a prerequisite for the subsequent multielectron

reduction reaction. Our first approach is to use diffusion reflectance infrared Fourier-transform spectroscopy (DRIFTS) to study the adsorption behavior of the catalysts towards the CO_2^+ . Fig. S31a shows two bands at 2349.54 and 2353.50 cm^{-1} associated with the stretching vibration of $^*\text{CO}_2$. In contrast, when NTP-treated CO_2 gas is used as the adsorbed gas, the infrared characteristic peaks move in a direction of low wavenumber, and their intensity increases with prolonged adsorption (Fig. S31b). Furthermore, the CO_2^+ temperature-programmed desorption (TPD) of the as-prepared samples can prove the similar results, as displayed in Fig. S32a. The chemical CO_2^+ desorption signal strength for the InCZ-2 sample is higher than those of the InCZ-1, In-1, In-2 and CZS samples, indicating that the InCZ-2 sample hints at a potential advantage in efficient CO_2^+ capture and release. It is noteworthy that CZS exhibits a lower CO_2^+ desorption temperature, which indicates that pure $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ has a weak adsorption of CO_2^+ . A further test was conducted to determine the performance of the photocatalysts in terms of CO adsorption and desorption. As illustrated in Fig. S32b, all samples exhibit lower CO gas desorption signal peaks as the progressive temperature ramp. In particular, pure CZS and composite samples (InCZ-1, InCZ-2) containing $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ show weak CO gas adsorption, indicating limited CO desorption. Accordingly, CO gas is not capable of facilitating photocatalytic CO_2 reduction to yield C_2 . The above experimental phenomenon shows that CO_2^+ can be strongly adsorbed by the active sites on the catalyst surface [30]. Thus, identifying the type and mechanism of active sites can assist us in understanding the mechanism of CRR. Firstly,

we developed the heterostructure of the In_2O_3 (222) and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ (101) crystal planes based on the HRTEM and TEM test results (Fig. S33) and screened all possible transition metal active sites (Cd and Zn) on the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ (101) crystal plane by using DFT calculations. As shown in Fig. S34, the Cd atoms in a crystal plane (101) cannot interact with CO_2^+ , whereas the Zn atoms can interact with CO_2^+ in a vertical configuration. Adsorption energy ($E_{\text{ad}} = E_{\text{total}} - (E_{(101)} + E_{\text{CO}_2^+})$) refers to the energy released by CO_2^+ adsorption. In $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$, $E_{(101)}$ represents the total energy of the (101) crystal plane, while $E_{\text{CO}_2^+}$ represents the total energy of a relaxed CO_2^+ . In Fig. S35, the adsorption energy of CO_2^+ is determined by DFT calculations based on the above formula, which indicates that the Zn active sites of the (101) crystal plane exhibit excellent adsorption properties for CO_2^+ ($E_{\text{ad}} = -0.49$ eV).

To further elaborate on the adsorption properties, we compare the orbital resolved pDOS of CO_2^+ bonding features at Zn sites. As shown in Fig. 4a, the energy levels (3d and 4s orbitals) of Zn in $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ (101) are lower than those in CO_2^+ σ orbitals. So, it cannot produce locally occupied d- σ (occ) orbitals with adsorbed CO_2^+ , which is different from the mechanism of traditional transition metal activation. Nevertheless, the energy level of the lone pair electrons and π in the CO_2^+ is higher than that of the 4s orbital of Zn, allowing the lone pair electrons and π electrons to be injected into Zn's empty 4s orbital, forming 2p-4s and 2-4s orbital interactions. Thus, it weakens the delocalized π bond in CO_2^+ and realizes efficient activation of CO_2^+ . As shown in Fig. 4b, the crystal orbital Hamiltonian population curves (COHP) for CO_2^+ adsorbed on InCZ-2 are shown as well as the integrated values (ICOHP). More negative ICOHP indicates stronger Zn- CO_2^+ coupling. As a result, the electrons in the $\pi_{(2p_z)}$ and lone pair (2s orbital) of CO_2^+ have the

strongest interactions with the 4s empty orbital of Zn (with the highest ICOHP value), whereas the electrons in the 3d orbit of Zn exhibit little interaction [31]. Furthermore, as for CO_2^+ , lone pairs can donate electrons to the empty 4s orbital of the reaction sites in Fig. 4b (inset images). These results can be verified by the electron location function and charge density distribution of CO_2^+ absorption on the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ (101) crystal plane (Fig. S36). In general, the catalytic interaction between CO_2^+ and the Zn active site is associated with the "acceptance donation" of electrons, where controlling the delocalized $\pi_{(2p_z)}$ orbitals electrons and lone pair electrons of the CO_2^+ is crucial for accelerating NTP-assisted CRR process.

In situ diffuse reflectance infrared Fourier-transform (DRIFTS) spectroscopy monitors the above reaction process. Fig. 4c shows the in situ (DRIFTS) spectra obtained during the CRR under the NTP condition at increased irradiation times. It is noteworthy that peaks at 1339, 1647 and 1654 cm^{-1} are assigned to stretching of adsorbed $^*\text{OCOH}$. The presence of peaks at 1457, 1472, 1507, 1522, and 1541 cm^{-1} ($m\text{-CO}_3^-$) is essential evidence of surface-absorbed $^*\text{OCOH}$ species. Notably, the critical intermediate $^*\text{OCHCO}$ intensity at 1716 cm^{-1} increases with increasing irradiation time, signifying C_2 product formation [32,33]. Moreover, in situ Raman spectroscopy has revealed a peak at 1484 cm^{-1} that corresponds to the C-O stretching vibration of carboxylate $^*\text{OCH}$ (Fig. S37) [2]. This intermediate is the first step in forming $^*\text{OCHCO}$, providing solid evidence to prove the synthesis of C_2 products. In addition, we conduct a DRIFTS spectrum test of CO_2 reduction activity without NTP assistance. Only a few reaction intermediates are detected on InCZ-2, suggesting it is difficult for CO_2 to react with the catalyst to produce C_2 products (Fig. S38). Based on the above results, it is possible

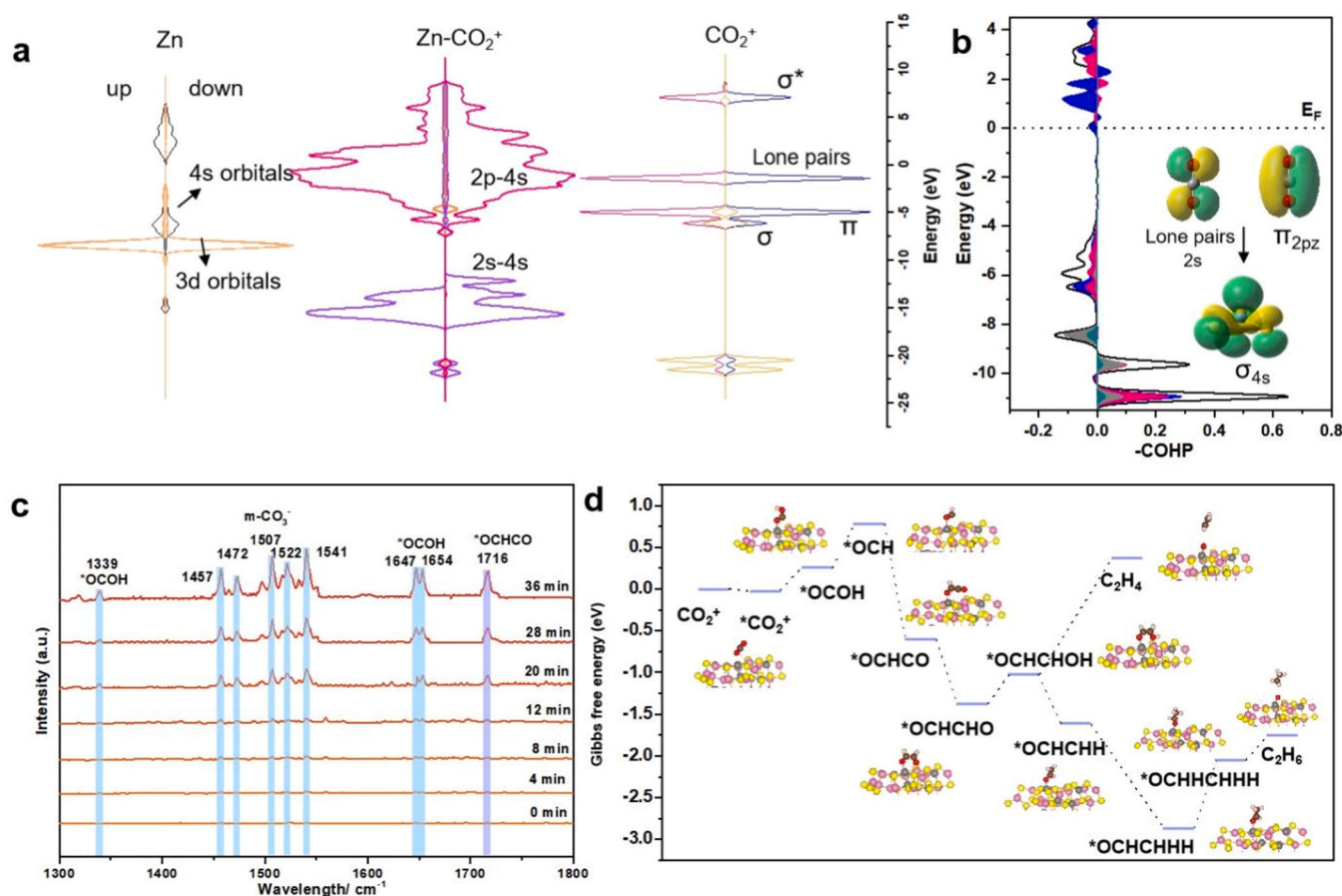


Fig. 4. a) Projected electronic density of states (pDOS) and the orbital distributions of 3d orbitals of Zn active sites, the orbitals of $^*\text{CO}_2^+$ adsorbed on Zn active sites and 2p orbitals of CO_2^+ , respectively. b) COHP analysis of the Zn-O bonding interactions and CO_2^+ provides electrons to the empty 4s orbital. c) In situ DRIFT spectra of the InCZ-2 sample. d) Gibbs free energy diagrams and CO_2^+ to C_2H_4 and C_2H_6 photoreduction pathway on Zn active sites.

to conclude that the CRR process under the NTP condition exhibits excellent performance due to the interaction between $^*\text{CO}_2^-$ and Zn active sites. The Gibbs free energy diagrams calculated by DFT are useful in proving the reaction pathway and intermediate configurations of the NTP-assisted CRR process. Zinc atoms as active sites in the (101) crystal plane can interact with CO_2^- with a vertical absorption configuration (Fig. S39). Fig. 4d illustrates the Gibbs free energy diagrams of NTP-assisted CRR on Zn active sites. In the first step, the CO_2^- on the heterojunction surface is easily activated to generate adsorbed $^*\text{CO}_2^-$, which is subsequently converted uphill into $^*\text{OCOH}$ and $^*\text{OCH}$ [34,35]. Afterward, the transition from $^*\text{OCH}$ to $^*\text{OCHCO}$ shows a lower uphill energy barrier, indicating that the C-C coupling step has little influence on the reaction. This explains the higher productivity of C_2 products on InCZ-2 in CRR. Then, the reduction energy barrier from $^*\text{OCHCO}$ to $^*\text{OCHCHO}$ is thermodynamically favorable with an energy release of 0.77 eV. With multi-step hydrogenation steps in the pathway, the production of C_2H_4 displays the greatest energy barrier ($\Delta G=1.98$ eV), illustrating the difficulty of desorbing ethylene. However, the production of ethane gas has a ΔG of 0.29 eV, which is far lower than ethylene production's energy barrier. Overall, the energy expenditure from $^*\text{OCHCHO}$ to C_2H_4 is higher than that from $^*\text{OCHHCHHH}$ to C_2H_6 , further verifying the yield ranking of $\text{C}_2\text{H}_6 > \text{C}_2\text{H}_4$, which is consistent with the quantum efficiency and pCRR activity results. Taken together, it is evident from these experimental and calculated results synergistically that CO_2^- can be readily activated on Zn sites and that C_2H_4 gas desorption is a rate-determining step in the reaction pathway.

4. Conclusion

This work would enrich our knowledge in designing efficient photocatalysts for photocatalytic nitrogen reduction. In summary, a demonstrated photocatalytic CO_2 conversion into C_2 products under NTP enables facile CO_2^- absorption and efficient ethylene and ethane production in two-stage synergistic systems. A developed nanoconfined $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}/\text{In}_2\text{O}_3$ photocatalyst with a long photo-electrons lifetime exhibits a significant C_2 products yield of $0.382 \mu\text{mol h}^{-1}$, respectively. Combining a series of in situ measurements and DFT calculations reveals an "acceptance donation" reaction mechanism for NTP-assisted CRR on Zinc-based nanoconfined photocatalysts. A high-energy plasma electric field produces CO_2^- . The 4 s orbitals of Zn active sites can accept the lone pair electrons and $\pi(2p_z)$ orbitals electrons of CO_2^- . This brand-new "acceptance donation" phenomenon leads to excellent performance and selectivity for photocatalytic CRR to C_2H_4 and C_2H_6 . This work provides new insights and opportunities for manufacturing carbon-neutral energy.

CRedit authorship contribution statement

He Li: Methodology, Investigation. **Mengyang Xia:** Formal analysis. **Xiaxin Wang:** Visualization. **Ben Chong:** Validation. **Honghui Ou:** Investigation. **Bo Lin:** Data curation. **Guidong Yang:** Investigation, Writing-Review & Editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2023.123423.

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